Theses and Dissertations	1. Thesis and Dissertation Collection, all items

1966

Infrared spectra of HOH, DOD, and HOD in non-polar solvents.

Morris, Harold Dean.

Monterey, California. U.S. Naval Postgraduate School

http://hdl.handle.net/10945/9538

INFRARED SPECTRA OF HOH, DOD,
AND HOD IN NON-POLAR SOLVENTS

HAROLD DEAN MORRIS

INFRARED SPECTRA OF HOH, DOD,

AND HOD IN NON-POLAR SOLVENTS

by

Harold Dean Morris
Lieutenant, United States Navy
B.S., California Institute of Technology, 1958

Submitted in partial fulfillment
for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the

UNITED STATES NAVAL POSTGRADUATE SCHOOL
December 1966

ABSTRACT

The infrared vibrational spectra of HOD and DOD dissolved in carbon
tetrachloride and carbon disulfide were obtained and compared with the
same spectra of HOH. The spectra of these three water species were com-
pared to those of the vapors and the similarities noted. The bending
mode, γ_2, of DOD in carbon disulfide was observed. Temperature effects
on the spectra were also studied. To analyze the data a simple theoret-
ical vibrational treatment was used providing a computation readily
adaptable to digital computers.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

1. Introduction

Infrared Spectra of HOH

The infrared spectrum of water has been intensively studied in vapor phase, liquid phase, and in dilute solutions of non-polar solvents. The vapor phase spectrum has been analyzed by many investigators and in considerable detail first by Darling and Dennison. [1]

The water molecule is well known to have the form of an isosceles triangle with equivalent OH bonds, an example of C_{2v} symmetry. Such a molecule possesses three normal modes of vibration, all of which should be active in both the infrared and Raman spectra. The H-O-H bond angle is reported to be 104.5 ± 0.10^O with an equilibrium bond distance of $0.9580 \overset{O}{A}$. [1-3] The bond angle of DOD is known to be identical. [4]

Benedict, Gailar and Plyler present the most recent definitive infrared spectral data for HOH, giving the values of the fundamental water vapor vibrational frequencies as: γ_1 = 3656.65 cm^{-1}, γ_2 = 1594.56 cm^{-1}, and γ_3 = 3755.79 cm^{-1}. [4] These vibrational modes may be depicted with reasonable accuracy as shown in Figure A.

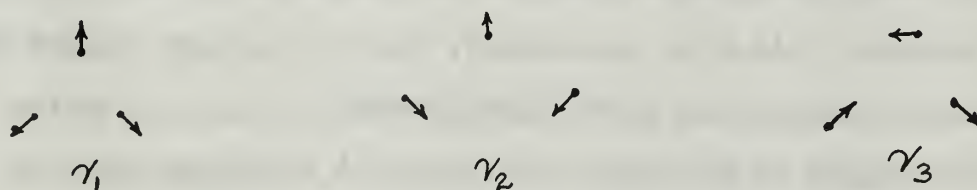$$\gamma_1 \qquad \gamma_2 \qquad \gamma_3$$

Figure A

Herzberg summarizes previous values of infrared and Raman data for the various water molecules HOH, HOD, and DOD.

Liquid water exhibits the characteristic very broad, intense infrared absorption found for hydroxy containing compounds such as alcohols

and carboxylic acids. This band is attributed to associated or hydrogen bonded species.[6]

Infrared Spectra of Water in Non-Polar Solvents

Upon dilution of the OH containing compounds with non-polar solvents such as carbon tetrachloride or carbon disulfide, a new, narrow absorption band appears at a higher frequency than that of the original associated species. [7-9] This new absorption is assigned to the stretching frequency of the unassociated OH bond.

Infrared spectra of dilute solutions of HOH in carbon tetrachloride were studied by Borst et al., who observed two absorptions in the OH stretching region at 3702 cm^{-1} and 3611 cm^{-1}. [10] These investigators suggested that the 3702 cm^{-1} absorption be assigned to γ_3 and the 3611 cm^{-1} band to γ_1. Later Fox and Martin confirmed these observations at frequencies of 3705 cm^{-1} and 3614 cm^{-1} and stated that these absorptions were, respectively, the γ_3 and γ_1 vibrations of the monomeric HOH species in carbon tetrachloride solution. [11] Reisinger has confirmed these observations assigning 3705 cm^{-1} to γ_3 and 3613 cm^{-1} to γ_1. [12] None of these investigators reported an observation of the γ_2 or bending frequency. This is to be expected, since in the path lengths used for these investigations carbon tetrachloride and carbon disulfide absorb intensely in the region near 1595 cm^{-1}, the vapor phase γ_2 frequency.

To avoid these solvent absorptions the present investigation utilized DOD and HOD whose gas phase γ_2 frequencies are 1178 cm^{-1} and 1402 cm^{-1} respectively. This yielded an interference free spectrum only for the ν_2 mode of DOD in carbon disulfide, the γ_2 of HOD being obscured in all solvents used.

Fox and Martin were able to separate graphically a third band in the HOH spectrum centered near 3810 cm^{-1}. [11] Noting that this absorption appeared to follow the general shape of rotation lines in this region they proposed that this absorption was the envelope of the rotation lines. Reisinger also noted this third band placing it at 3804 cm^{-1}. [12] Additionally, he separated a fourth absorption in this region centered at 3540 cm^{-1}. These third and fourth absorptions were also noted by Reisinger in an investigation of a dilute solution of HOH in carbon disulfide. [12] The nature of the absorptions appeared identical to those of HOH in carbon tetrachloride except for a slight shift of the frequencies to 3796 cm^{-1} and 3547 cm^{-1}. Earlier investigators do not indicate that their studies covered the low frequency region (near 3500 cm^{-1}) so that this fourth band (3540 cm^{-1}) was unobserved by them. [11]

The γ_2 frequency for HOH in carbon tetrachloride and carbon disulfide would be expected at about 1595 cm^{-1} (the vapor phase γ_2) since, as is reported later, the γ_2 frequency for DOD in carbon disulfide is very little shifted from its vapor phase value of 1178 cm^{-1}. However, γ_2 has not been observed for HOH in carbon tetrachloride or carbon disulfide.

Temperature Effects

Early investigators of the spectra of OH bearing species noted that the relative intensities of the OH stretching absorptions were functions of temperature. They attributed the effect to temperature induced changes in monomer-polymer equilibrium or to solvent effects, i.e., a change in the molar absorption coefficient. [8,13]

More recently, however, Slowinski and Claver have noted that for pure liquids the intensities of OH stretching absorptions as well as

C-H, C-Cl and other bond stretching absorptions depend markedly on temperature. [14] These workers show clearly that both the maximum optical densities and the integrated intensities of these stretching absorptions decrease with rising temperature. Their work was rapidly followed by the efforts of other investigators who have extended and refined these observations, studying hydrogen bonded equilibria in dilute solutions. [15,16] Hughes, Martin, and Coggeshall demonstrate that the intensity of the absorbance of the unassociated OH stretching bond decreases linearly with increasing temperature. [15]

Calculations

The theoretical bases for correlating vibrational frequencies of molecules with their parameters (masses and geometries) has been known for many years. Wilson, Decius, and Cross have thoroughly delineated the methods for these calculations. [17] The matrix methods presented by these authors are readily adapted to digital computer technology and presented an opportunity to determine if there was a simple theoretical vibrational treatment consistent with the results of this investigation. In one simple treatment of a non-linear triatomic molecule such as water, the three fundamental vibrational frequencies are determined by four force constants and the molecular parameters. These three frequencies are, of course, insufficient information for solution of the equations determining the four force constants. However, application of the Born-Oppenheimer approximation permits the assumption that the potential function is unchanged by isotopic substitution. This allows the six fundamental vibrational frequencies of HOD and DOD to be used in determining these same force constants. In the two calculations made here the first used the five observed frequencies of HOH and DOD.

The second used, in addition, the two observed frequencies of HOD for a total of seven.

2. Experimental

Infrared Absorption of the Water Molecules HOH, DOD, and HOD

The Perkin-Elmer Model 221 recording spectrometer with a sodium chloride prism-grating combination was used in the double beam mode of operation. The spectrometer was calibrated in the regions of interest using the vapor phase spectra of HCl, HBr, NH_3, CO_2, and HOH as indicated in Table I. The pressures were chosen for the purpose of direct comparison with the reference values given by the Commission on Molecular Spectroscopy. [18] All gases used except the HOH were Matheson Co. bottled gases. The HOH spectrum was obtained from atmospheric vapor using the spectrometer in single beam operation. The standard deviations from the mean of the observed frequencies are given in Table I for each range. A mean correction was determined for each range and applied to the observations to yield the reported values.

Connecticut Instrument Corporation 50 mm path length glass cells were used with BaF_2 windows. These cells have a capacity of approximately 30 ml. Only glass, Teflon, and BaF_2 were in contact with the sample in these cells.

The carbon tetrachloride and carbon disulfide used as solvents were Fisher Scientific Co. spectral grade reagents. No additional purification was necessary. It was necessary to dry the solvents as completely as possible using the disappearance of the γ_3 and γ_1 HOH frequencies as a minimum criterion of dryness. Previous investigators have used a variety of techniques for drying, most of which proved unsatisfactory when used in this laboratory. [9,12,19] These included drying over $CaCl_2$, Na_2SO_3, Na_2SO_4, bubbling with dry air, and distillation. P_2O_5 was a successful drying agent, but its use involves consid-

TABLE I

Calibration Data

Standard	Frequency (cm^{-1})	(cm^{-1})	Pressure (mm)
HCl	2680-2900	0.5	120
HBr	2600-2720	0.5	140
NH_3	1160-1200	0.3	50
H_2O	3745	0.9	*
CO_2	3620	0.9	400

* Atmospheric vapor

erable tedious handling. Linde Co. type 4A molecular sieve in bead form was used in this investigation, the beads being placed directly in a glass stoppered bottle of the solvent. In order to prevent leakage of moisture into the sample, the bottle was placed in a dessicator containing P_2O_5. No change was observed in the dried solvents or the molecular sieve. The solvent spectra were also unchanged over the region 4000 to 750 cm^{-1} except, of course, for the HOH bands. All transfers were made using a syringe to minimize contact with atmospheric moisture.

Dry carbon tetrachloride with a small amount of added DOD produced an observable HOD absorption in as short a time as fifteen minutes when placed in the glass-stoppered BaF_2 cell. However, dry carbon tetrachloride alone did not produce an HOH absorption for a minimum of several times as long. It was proposed that exchange of D for H with the glass cells may have been responsible for this phenomenon. To prevent contamination by absorption of atmospheric moisture a few granules of molecular sieve were placed in the dry reference cell sample. This

effectively prevented contamination during a span of several hours, which was the longest period observed. All spectra were recorded with an identical cell filled with dry solvent inserted in the reference beam of the spectrometer.

Saturated solutions of HOH and DOD in both solvents were prepared by adding excess HOH or DOD to the dried solvent and allowing a minimum of 24 hours for equilibration. The DOD was obtained from Bio-Rad Laboratories and stated to be 99.83 mole percent DOD.

The various sample solutions were prepared as a given percent of saturation by dilution of the saturated solution with dry solvent.

The equilibrium for the reaction

$$HOH + DOD \rightleftarrows 2\ HOD \qquad \text{with} \qquad K = \frac{[HOD]^2}{[HOH]\ [DOD]}$$
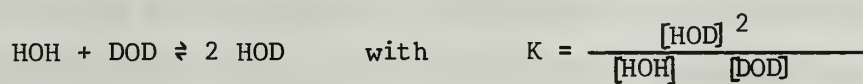
is known to be very rapid. The equilibrium constant has been determined as $K = 3.96$ at 25°C. [20] For a given sample we have

$$[HOD] + [HOH] + [DOD] + C$$

where C is a constant. Noting that

$$[HOD]^2 = K\ [HOH]\ [DOD]$$

it can be seen that the condition for HOD to be a maximum is

$$[HOH] = [DOD].$$

So then

$$[HOD]_{max} = \frac{\sqrt{K}}{2 + \sqrt{K}}$$

and for $K = 3.96$ the maximum $[HOD]$ is about 50 mole percent, which is a ratio of 1:2:1 for the various water species. This maximum HOD concentration exists for an equimolal mixture of HOH and DOD. The values in Table II give the observed frequencies for the HOD spectrum in carbon tetrachloride. The notation of Benedict et al. has been adopted

TABLE II

Frequencies of vibrational absorptions of various species of water (in cm^{-1})

Vapor Phase

	HOH	DOD	HOD
ν_1	3657	2671	2727
ν_2	1595	1178	1402
ν_3	3756	2788	3707

Carbon Tetrachloride Solutions

	HOH	DOD	HOD
ν_1	3614	2642	2692
ν_2	-	-	-
ν_3	3705	2751	3660

Carbon Disulfide Solution

	HOH	DOD
ν_1	3603	2635
ν_2	-	1180
ν_3	3695	2744

Values given for vapor phase spectra are those of Benedict et. al. (rounded to the nearest cm^{-1}). [4]

in describing the HOD vibrational bands, namely γ_1 = OD stretching, γ_2 = bending, and γ_3 = OH stretching vibrations. [4]

There is considerable overlap of the γ_1 HOD frequency, 2692 cm^{-1}, with those of the DOD spectrum and of the γ_3 HOD frequency, 3660 cm^{-1}, with the HOH spectrum. Consequently, the optimum concentration of HOD is one that will minimize the interfering bands while allowing sufficient intensity of the HOD absorption. A 9:1 misture of HOH and DOD will yield approximately an 81:18:1 ratio of HOH:HOD:DOD. This 18:1 ratio of HOD to an interfering species is an order of magnitude improvement over the previous ratio of 2:1 at maximum mole percent HOD.

Temperature Effects

In order to observe the effect of temperature on the spectra special cells were constructed. These were 50 mm path length glass cells with a coolant jacket as an integral part of the cell. Water from a constant temperature bath was used as the regulating fluid. Silver chloride windows were held in place on the ends of the cell body by aluminum discs fastened to each other with screws. Internal cell temperatures were measured with a thermocouple. Carbon tetrachloride solutions were studied over a range from 3°C to 60°C. Due to the high vapor pressure encountered in this temperature range, carbon disulfide solutions were not studied.

Figure 1

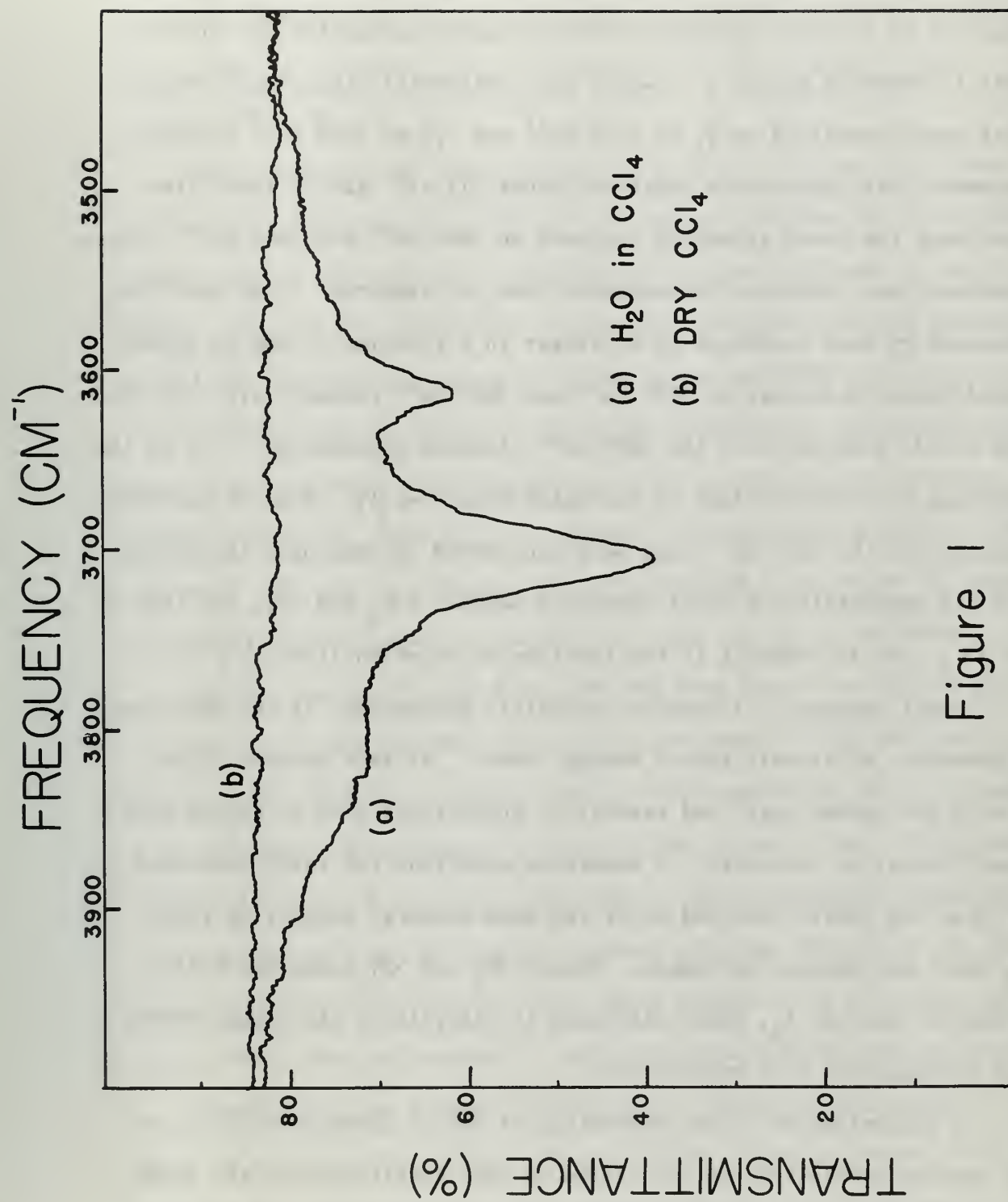(a) H_2O in CCl_4

(b) DRY CCl_4

FREQUENCY (CM⁻¹)

TRANSMITTANCE (%)

3. Results and Discussion

The results of earlier workers were confirmed upon analysis of the spectrum of a dilute solution of HOH in carbon tetrachloride. [10-12] This is shown in Figure 1. Two of the fundamental vibrational frequencies were identified as γ_1 at 3614 cm^{-1} and γ_3 at 3705 cm^{-1} in close agreement with previously reported values. [11,12] Easily identified also were the broad sidebands centered at 3804 cm^{-1} and 3540 cm^{-1}. These sidebands were graphically separated from the spectrum. They were also observed by this technique by Reisinger in a solution of HOH in carbon disulfide with centers at 3796 cm^{-1} and 3547 cm^{-1} respectively. [12] Fox and Martin observed only the 3804 cm^{-1} sideband considering it to be the envelope of rotation lines of the water molecule. [11] Several possible sources for the 3540 cm^{-1} band were considered by Reisinger including: (1) the possibility of Fermi resonance between $2\gamma_2$ and γ_1, (2) that it is $2\gamma_2$, and (3) that it is the envelope of rotation lines. [12]

Fermi resonance, a quantum mechanical phenomenon, is the result of interaction of closely spaced energy levels. In this process these levels are spread apart and associated transitions tend to become more nearly equal in intensity. A necessary condition for Fermi resonance is that the levels involved be of the same symmetry species or share at least one species in common. Since $2\gamma_2$ and γ_1 share the fully symmetric species A_1, Fermi resonance is possible if the energy levels are sufficiently near one another.

A determination of the absorption of DOD in carbon tetrachloride at varying percentages of saturation at 28°C confirmed that the bands at 2751 cm^{-1} and 2642 cm^{-1} should be assigned to the γ_3 and γ_1 frequencies of the DOD molecule. These results are shown in Figure 2. It

is observed that the structure of the DOD absorption is completely anal-
ogous to that for HOH including the two low intensity sidebands. The
spectrum of HOD in carbon tetrachloride shown in Figure 3 for an eighteen
to one HOD to DOD mixture is also observed to have the same basic
structure for γ_1 and γ_3.

Since the solvents investigated are opaque in the region of the
HOH bending vibration near 1595 cm^{-1}, a search was made for the bending
frequencies of DOD and HOD. The HOD bending mode was found to be ob-
scured in 50 mm path lengths of both carbon tetrachloride and carbon
disulfide. For DOD in carbon disulfide it was possible to observe a
low frequency band at 1180 cm^{-1} which was assigned as the bending vibra-
tion, γ_2. In view of this appearance of γ_2 very close to the gas
phase frequency of 1178 cm^{-1}, it appears that the bending vibration of
the water molecule is almost entirely unaffected by solution in carbon
tetrachloride and probably therefore in other non-polar solvents.

Hornig, using infrared data obtained from systems of dilute HOD
in both liquid HOH and DOD, states that the shape of the HOH absorp-
tions in the stretching regions results from overlap of γ_1, γ_3, and
2 γ_2, and that the intensity variations are caused by Fermi resonance
between 2 γ_2 and γ_1. [21,22] This type of system exhibits a decrease
of about 300 cm^{-1} in γ_1, and an increase of about 50 cm^{-1} in γ_2 when
compared to gas phase frequencies. These shifts bring 2 γ_2, and γ_1
sufficiently near one another to allow the possibility of Fermi resonance.

Considering the present case of HOH in carbon tetrachloride, it
seems by analogy with DOD in carbon disulfide, that the shift of γ_2
from its gas phase frequency is essentially zero. The shift of γ_1 is
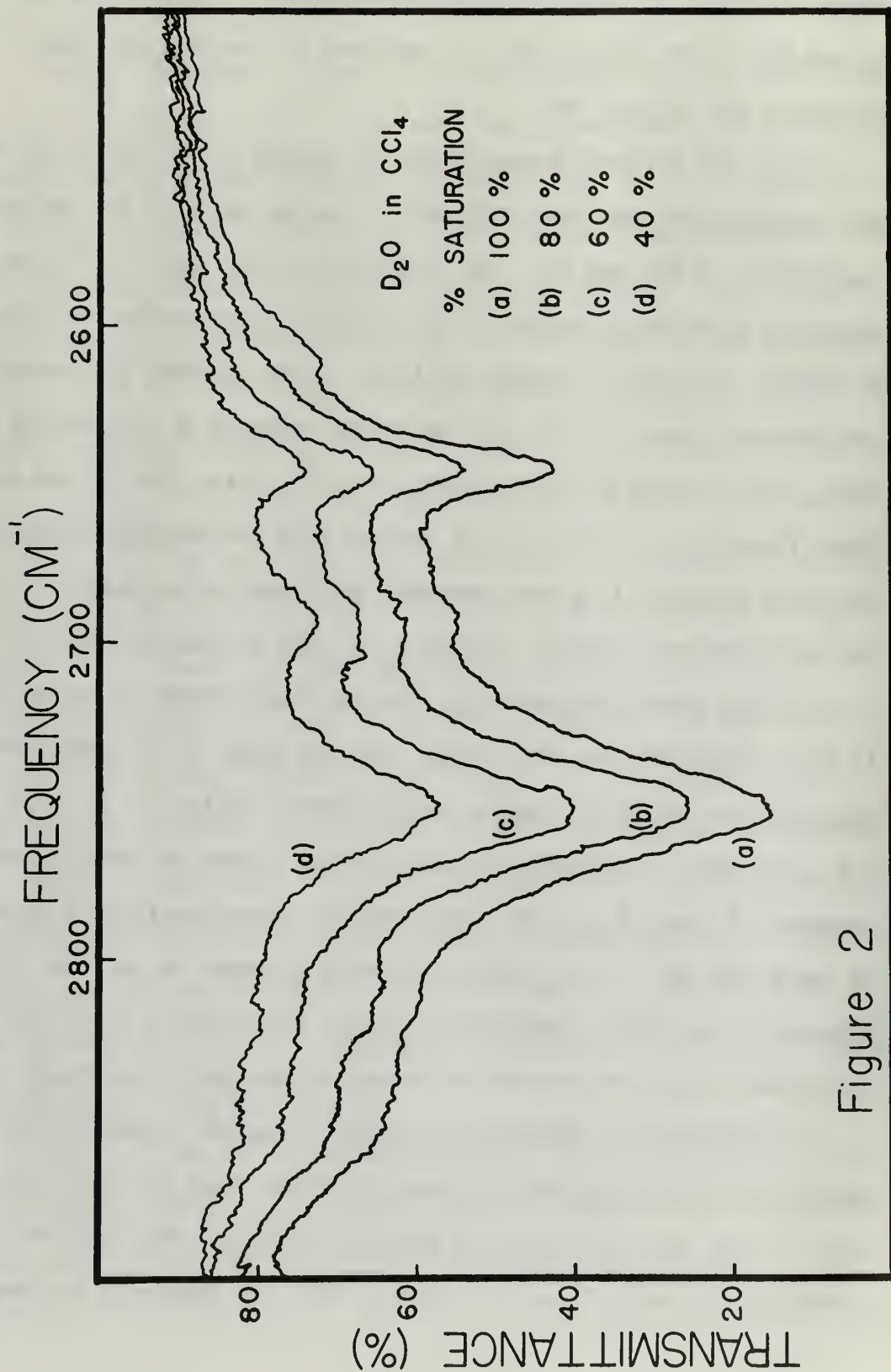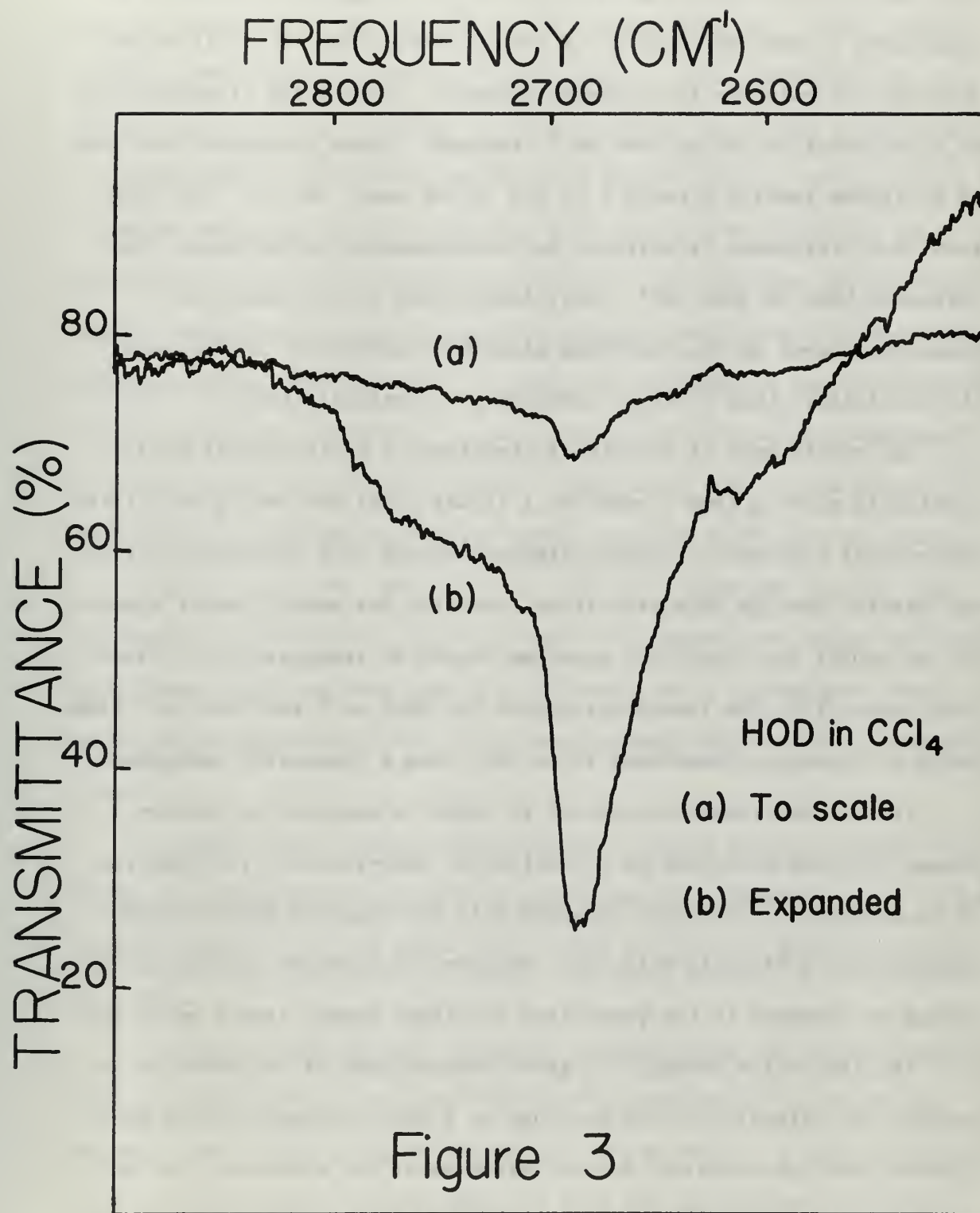a decrease of about 50 cm^{-1}. The 2 γ_2 mode for HOH vapor is observed

Figure 2

FREQUENCY (CM')

TRANSMITTANCE (%)

HOD in CCl$_4$

(a) To scale

(b) Expanded

Figure 3

at 3151 cm^{-1}, lowered from the harmonic potential value of 3190 cm^{-1}.
Considering the unshifted position of γ_2 in non-polar solvents it is
reasonable to conclude that it is very unlikely that $2\gamma_2$ will exceed
3190 cm^{-1} in solution in non-polar solvents. This would eliminate $2\gamma_2$
as an explanation of the 3540 cm^{-1} sideband. These considerations lead
to a minimum spacing between $2\gamma_2$ and γ_1 of about 400 cm^{-1} implying
that Fermi resonance is unlikely as an explanation of the broad, low
intensity band at 3540 cm^{-1}. This disposition of $2\gamma_2$ and Fermi
resonance leaves as the remaining plausible explanation of the band
the possibility that it is an envelope of rotational lines.

The persistance of rotational structure of a vibrational band of
a molecule passing from a vapor to a liquid phase has been given little
theoretical treatment. Longuet-Higgins expects that hindered rotation
may persist through this transition, and that for small, nearly spheri-
cal molecules the rotational envelope should be recognizable in favor-
able cases. [23] The interpretation of the 3804 cm^{-1} and 3540 cm^{-1} side-
bands as rotational envelopes is in this view a reasonable assignment.

If this assignment is correct it might be possible to observe a
change in these envelopes as a function of temperature. The spectrum
of an asymmetric rotor such as water will not show the simple changes
observed for a diatomic molecule. However, an increase in temperature
giving an increase in the population of higher energy levels would pro-
duce the same basic change in a gross feature such as the rotation en-
velope; an extension of the envelope to a wider frequency range with
greater relative intensity for the extremes of the envelope. In con-
trast to this expected increase of intensity with temperature, the re-
sults of Hughes et al. (that the intensity of the OH absorbance decreases

with increasing temperature) leads to the possibility of either an increase or decrease. [15] In fact, no change in intensity of the envelope was was identified over the 3°C to 60°C range observed. Some tentative changes were noted but were not reproducible. The intensities of the vibrational absorption maxima did decrease with increasing temperature in approximately the manner described by Hughes for all three species of water molecules in both solvents. [15] Due to the difficulty of accurately measuring integrated intensities, only maximum optical densities were noted. Using the cells described, maintenance of a uniform temperature was not possible. It would be desirable to use an apparatus of the type used by Hughes: a specially constructed metal compartment which maintains an accurate, uniform temperature over a wide range. [15] Some manner of sealing the system under pressure would also be useful.

The fact that the 3804 cm^{-1} and 3540 cm^{-1} sidebands did not show a detectable decrease of intensity over this temperature range indicates that these bands are very probably not overtone or combination bands since the temperature effect would have markedly reduced their intensities.

It seems, then, that although there is little direct evidence that these two sidebands are rotational envelopes, the dismissal of all other proposed sources for the bands leaves this as the most probably interpretation.

The hygroscopic natures of carbon tetrachloride and carbon disulfide are exhibited in the great difficulty encountered in drying the solvents and in the rapid re-absorption of the water. A glass stoppered cell of carbon tetrachloride began to show HOH absorptions in periods on the order of one hour. Almost paradoxically, however, the solvent is

23

saturated by a mere one part in 10^4 of water. [19] The tenacious grip
of carbon tetrachloride and carbon disulfide on water may well be ex-
plained by interstitial trapping. Such a mechanism would reconcile the
observed difficulty in removing trace amounts of water with the low
solubility while also allowing the water molecule to remain essentially
free of interactions.

A normal coordinate analysis of the data was performed using the
methods of Wilson, Decius, and Cross. [17] The experimental values of
the fundamental vibration frequencies were used to calculate the quad-
ratic force constants in the potential energy expression. The constants
treated are those for a modified valence force treatment. In the case
of water, there are four constants. These are for OH bond stretching,
H-O-H bond angle deformation, and two constants for bond interactions
(stretch-stretch and bend-stretch). That this treatment is approximate
will readily be seen by noting that anharmonicity terms (cubic, quartic,
etc.) are omitted from the potential energy. Calculation of precise
quadratic force constants requires the use of "mechanical" frequencies
of vibration, the frequencies which would be observed if there were no
anharmonic terms in the potential energy. This calculation requires a
substantial quantity of data regarding overtone and combination levels
of the molecule and was accomplished for HOH vapor originally by Darling
and Dennison. [1]

The four valence force constants were computed here using five fre-
quencies (ν_1 and ν_3 of HOH, ν_1, ν_2, and ν_3 of DOD) and alternately
with seven frequencies, (the original five plus ν_1 and ν_3 for HOD).
A best fit for each calculation was obtained using a least squares tech-
nique. The computation was performed on a Control Data Corporation 1604

TABLE III

Results of Calculations

All Frequencies in cm^{-1}

Species	Mode	Observed	Calculated A	Calculated B
HOH	γ_1	3614	3608	3617
	ν_3	3705	3721	3705
DOD	γ_1	2642	2645	2646
	ν_2	1180	1180	1180
	γ_3	2751	2725	2751
HOD	γ_1	2692	2704	--
	ν_3	3660	3655	--

Force Constants*

Constant	A	B	C
	7.24	4.67	8.43
	0.92	3.39	0.77
	0.07	-2.50	-0.10
	-0.68	-0.84	0.25

*Units: Millidynes per Angstrom

Calculation A: Seven frequencies input (HOH, DOD, and HOD)

Calculation B: Five frequencies input (HOH and DOD only)

Calculation C: Given by Wilson, Decius and Cross as the mechanical frequencies for HOH. [17]

digital computer using FORTRAN 60 input. Details of the calculation are presented in the appendix. Results are presented in Table III.

All of the factors discussed above indicate the conclusion that the water molecule when dissolved in a non-polar solvent such as carbon tetrachloride or carbon disulfide interacts very weakly with the solvent. In summary these factors are:

(a) It has been shown that it is consistent with all observations to regard the 3804 cm^{-1} and 3540 cm^{-1} bands as envelopes of rotation lines, indicating that the molecules are relatively free to rotate;

(b) The very low frequency shifts observed upon change from vapor to condensed phase indicates that the potential field of the molecule is nearly undisturbed by molecular association;

(c) A calculation based on an unassociated molecule is reasonably consistent;

(d) The hygroscopicity of carbon tetrachloride and carbon disulfide is related to the low saturation value of water by a mechanism of interstitial trapping which is consistent with minimum molecular interactions.

ACKNOWLEDGEMENT

BIBLIOGRAPHY

1. B. T. Darling and D. M. Dennison, <u>Physical Review</u>, v. 57, 128, 1940.

2. D. W. Posener and M. W. P. Strandberg, <u>Physical Review</u>, v. 95, 374, 1954.

3. L. E. Sutton, Editor, <u>Tables of Interatomic Distances and Configurations in Molecules and Ions</u>, The Chemical Society, London, Burlington House, 1958.

4. W. S. Benedict, N. Gailar, and E. K. Plyler, <u>Journal of Chemical Physics</u>, v. 24, 1139, 1956.

5. G. Herzberg, <u>Infrared and Raman Spectra</u>, Van Nostrand, New York, 1945.

6. G. C. Pimentel and A. L. McClellan, <u>The Hydrogen Bond</u>, W. H. Freeman, 1960.

7. A. M. Buswell, V. Dietz, and W. H. Rodebush, <u>Journal of Chemical Physics</u>, v. 5, 84, 1937.

8. J. Errera and P. Mollet, <u>Nature</u>, London, v. 138, 882, 1936.

9. J. J. Fox and A. E. Martin, <u>Proceedings of the Royal Society</u>, v. A 162, 419, 1937.

10. L. B. Borst, A. M. Buswell, and W. H. Rodebush, <u>Journal of Chemical Physics</u>, v. 6, 61, 1938.

11. J. J. Fox and A. E. Martin, <u>Proceedings of the Royal Society</u>, v. A 174, 234, 1940.

12. J. E. Reisinger, <u>Thesis</u> (M. S.), Naval Postgraduate School, 1962.

13. M. M. Davies and G. B. B. M. Sutherland, <u>Journal of Chemical Physics</u>, v. 6, 767, 1938.

14. E. J. Slowinski and G. C. Claver, <u>Journal of the Optical Society of America</u>, v. 45, 396, 1955.

15. R. H. Hughes, R. J. Martin, and N. D. Coggeshall, <u>Journal of Chemical Physics</u>, v. 24, 489, 1956.

16. U. Liddel and E. D. Becker, <u>Journal of Chemical Physics</u>, v. 25, 173, 1956.

17. E. B. Wilson, J. C. Decius, and P. C. Cross, <u>Molecular Vibrations</u>, McGraw-Hill, 1955.

18. International Union of Pure and Applied Chemistry, Commission on Molecular Structure and Spectroscopy, _Tables of Wavenumbers for the Calibration of Infra-Red Spectrometers_, Butterworths, 1961.

19. C. W. Clifford, _Industrial and Engineering Chemistry_, v. 13, 631, 1931.

20. H. C. Urey, _Journal of the Chemical Society_, (London), 562, 1947.

21. D. F. Hornig, _Journal of Chemical Physics_, v. 40, 3119, 1964.

22. R. D. Waldron, _Journal of Chemical Physics_, v. 26, 809, 1957.

23. H. C. Longuet-Higgins, _Proceedings of the Royal Society_, v. A 255, 63, 1960.

The quadratic force constants for the potential energy expression

for the water molecule were calculated by fitting the calculated vibra-

tional frequencies to the observed frequencies by the method of least

squares. Calculated vibrational frequencies were obtained through

solution of the secular equation in the form given by Wilson, Decius

and Cross,

$$\left| \underset{\sim}{G} \underset{\sim}{F} - \underset{\sim}{E} \right| = 0$$

where G, E, and F are matrices. [17] $\underset{\sim}{G}$ is the Wilson G matrix given by

$$
\underset{\sim}{G} = \begin{vmatrix}
\mu_1 + \mu_3 & \mu_3 \cos \emptyset & \dfrac{-\mu_3 \sin \emptyset}{r} \\[2mm]
\mu_3 \cos \emptyset & \mu_2 + \mu_3 & \dfrac{-\mu_3 \sin \emptyset}{r} \\[2mm]
\dfrac{-\mu_3 \sin \emptyset}{r} & \dfrac{-\mu_3 \sin \emptyset}{r} & \dfrac{1}{r^2}\left[\mu_1 + \mu_2 + 2\mu_3(1 - \cos \emptyset)\right]
\end{vmatrix}
$$

for non-linear triatomic molecules such as HOH, DOD and HOD. $\underset{\sim}{F}$ is

the matrix of quadratic force constants. For water these constants

are f_r bond stretching; f_α , bond angle bending; f_{rr} stretching inter-

action; and $f_{r\alpha}$, stretch-bend interaction.

$$
\underset{\sim}{F} = \begin{vmatrix}
f_{r_1} & f_{r_1 r_2} & f_{r_1} \\[2mm]
f_{r_2 r_1} & f_{r_2} & f_{r_2 \alpha} \\[2mm]
f_{r_1 \alpha} & f_{r_2 \alpha} & f_\alpha
\end{vmatrix}
$$

$\underset{\sim}{E}$ is the third order identity matrix. The machine solution of the

equations is quite simple: enter with values for $\underset{\sim}{G}$ and $\underset{\sim}{F}$, perform

the indicated product and then diagonalize this product. The resulting

eigenvalues are the desired fundamental vibration frequencies.

The least square fit of data was derived as follows:

Solve the system of equations:

$$\frac{\partial}{\partial Z_j} \left[\sum_i (f_i - g_i)^2 \right] = 0$$

where g (Z_j) are calculated frequencies, f_i are observed frequencies and Z_j are the force constants. Differentiating:

$$- \sum_i 2(f_i - g_i) \frac{\partial g_i}{\partial Z_j} = 0$$

Expanding g_i in terms of Z_j:

$$g_i = g_i^o + \sum_k \frac{\partial g_i}{\partial Z_k} \Delta Z_k \qquad \text{neglecting higher terms so that}$$

$$\sum_i \left[f_i - g_i^o - \sum_k \frac{\partial g_i}{\partial Z_k} \Delta Z_k \right] \frac{\partial g_i}{\partial Z_j} = 0$$

Let

$$\frac{\partial g_i}{\partial Z_k} \equiv D_{ik}, \; \Delta Z_k = \Delta_k \; \text{ and } \; \epsilon_i \equiv f_i - g_i^o$$

Then

$$\sum_i \left[\epsilon_i - \sum_k D_{ik} \Delta_k \right] D_{ij} = 0$$

$$\sum_i \epsilon_i D_{ij} - \sum_{ik} D_{ik} \Delta_k D_{ij} = 0$$

$$\sum_i D_{ji}' \epsilon_i - \sum_{ik} D_{ji}' D_{ik} \Delta_k = 0$$

Thus

$$(D' \epsilon)_j - (D'D \Delta)_j = 0$$

$$\text{where now}$$

31

$(D'\epsilon)_j$ and $(D'D\Delta)$

are column matrices.

$(D'D)$ is a square matrix, hopefully with an inverse. Then

$$(D'D)^{-1}\, D'\epsilon \;-\; \Delta \;=\; 0$$

so that

$$\Delta \;=\; (D'D)^{-1}\, D'\epsilon$$

For the second iteration new force constants (Z_j) are

$$Z_{jnew} \;=\; Z_{jold} \;+\; \Delta \qquad \text{where all are column matrices.}$$

DISTRIBUTION LIST

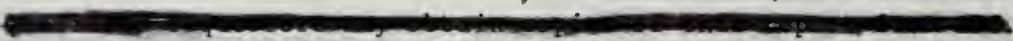No. Copies

1. Defense Documentation Center   20
    Cameron Station
    Alexandria, Virginia 22314

2. Library   2
    Naval Postgraduate School
    Monterey, California 93940

3. Prof. John W. Schultz   1
    Dept. of Material Science and Chemistry
    Naval Postgraduate School
    Monterey, California

4. LT Harold D. Morris, USN   1
    USS INDEPENDENCE (CVA-62)
    c/o Fleet Post Office
    New York, New York 09501

5. Prof. Glenn H. Spencer   1
    Dept. of Material Science and Chemistry
    Naval Postgraduate School
    Monterey, California 93940

6. Dept. of Material Science and Chemistry   2
    Naval Postgraduate School
    Monterey, California 93940

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Naval Postgraduate School Monterey, California	UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE

INFRARED SPECTRA OF HOH, DOD, AND HOD IN NON-POLAR SOLVENTS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Thesis, M.S., December 1966

5. AUTHOR(S) *(Last name, first name, initial)*

MORRIS, Harold Dean

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
December 1966	34	23

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. AVAILABILITY/LIMITATION NOTICES

This document has been approved for public release and sale; its distribution is unlimited

CoVe 12/19/65

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

The infrared vibrational spectra of HOD and DOD dissolved in carbon tetrachloride and carbon disulfide were obtained and compared with the same spectra of HOH. The spectra of these three water species were compared to those of the vapors and the similarities noted. The bending mode, ν_2, of DOD in carbon disulfide was observed. Temperature effects on the spectra were also studied. To analyze the data a simple theoretical vibrational treatment was used providing a computation readily adaptable to digital computers

DD FORM 1 JAN 64 **1473**

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Infrared						
Molecular						
Spectra						
Structure						
Vibration						
Water						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through

_____ ."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through

_____ ."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through

_____ ."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.